

In-Situ Deposition of YBCO High-T_c Superconducting Thin Films by MOCVD and PE-MOCVD

J. Zhao, D.W. Noh*, C. Chern**, Y.Q. Li*, P.E. Norris, B. Kear**, B. Gallois*
EMCORE Corporation, 35 Elizabeth Ave., Somerset, N.J. 08873

*Stevens Institute of Technology, Hoboken, NJ 07030

**Rutgers, The State University, New Brunswick, NJ 08854

The development of a successful low temperature, in-situ process for the formation of high temperature superconducting (HTSC) thin films is crucial for the early application of copper oxide-based ceramics. Such a process should permit the deposition of high quality, high density, HTSC films which have smooth surfaces, on a variety of substrates. Metal-Organic Chemical Vapor Deposition (MOCVD) process technology offers the advantages of a high degree of compositional control, adaptability for large scale production and the potential for low temperature fabrication. The capability of operating at high oxygen partial pressure is particularly suitable for in-situ formation of HTSC films. Use of a plasma-enhanced (PE) process substitutes electron kinetic energy for conventional thermal energy and enhances compound formation by introducing activated oxygen generated from dissociation of oxidizer constituents. This permits the use of lower temperature deposition conditions. In addition, the CVD process offers the advantage of easy transfer from R&D applications to low cost, large scale fabrication.

Our preliminary results demonstrate that high density, mirror smooth, low carbon YBCO films can be formed in-situ at reduced substrate temperatures, as low as 570°C. Further reductions in deposition temperature by increasing microwave plasma power are expected. Our results indicates that this method is a promising process for superconducting device technology.

Our approach involves the use of Metalorganic Chemical Vapor Deposition (MOCVD), which has been successfully employed in the production of III-V compound semiconductor devices. A novel variation on MOCVD, is the use of a microwave plasma to enhance the growth rate at low substrate temperatures. In addition, such a plasma-enhanced MOCVD (PE-MOCVD) process produces excited oxidizer species which, being more reactive than O₂, result in a higher degree of oxidation at low growth temperatures.

Comparisons of Deposition Techniques: PVD and CVD

To date, efforts to fabricate high T_c superconducting films at low temperature without post annealing have primarily involved activated physical vapor deposition (PVD) processes in which excited species were present such as plasma-assisted laser deposition,¹ activated reactive evaporation,² rf planar magnetron sputtering,³ and electron cyclotron resonance with oxygen plasma-assisted evaporation.⁴ These methods all have the drawbacks of requiring high vacuum, being limited to line-of-sight deposition, having low deposition rates, and having limited adaptability to flexible, large-scale production processes. Chemical Vapor Deposition (CVD), in principle, overcomes the above limitations. In addition, CVD offers accurate compositional control, through controlling the mass transport of individual precursors, and the fabrication of abrupt interfaces, due to the ability to rapidly change gas phase composition, which leads to the potential for creating metastable structures.

At the beginning of 1988, a few groups (including EMCORE)⁵ independently succeeded in the preparation of high T_c oxide films by MOCVD. In less than a year, Y-Ba-Cu-O films had been prepared with T_c higher than 90K and J_c = 1.9x10⁶ A/cm² at 77K,⁶ which is comparable to that obtained by PVD. Today, more than twenty research groups have joined this promising field which is currently dominated by the Japanese scientific community, with at

least ten laboratories active in the growth of HTSC thin-films using MOCVD. However, unlike PVD, no activated CVD method has been fully developed, hence, a deposition temperature of more than 800°C is still required to obtain high quality, in-situ HTSC films using MOCVD. However, YBCO films can be formed at temperatures around 600°C using activated PVD.^{1,2} Due to the strong chemical reactivity of HTSC materials, a deposition temperature around 600°C is still too high to prepare superconducting thin films on some technologically important, but more highly reactive substrates, such as Si.

MOCVD, which has the capability of operating at high oxygen partial pressure, is particularly suitable for in-situ formation of HTSC films. Fig.1 shows a plot of oxygen partial pressure vs. temperature indicating the location of the phase transitions of $\text{YBa}_2\text{Cu}_3\text{O}_y$ together with experimental data points from the literature⁷ for several reports of successful in-situ growth. The critical phase stability boundary is at $y = 6.0$. Below $y=6.0$, YBCO is unstable and disproportionates into Y_2BaCuO_5 , BaCuO_2 and Cu_2O . At an oxygen content of 6.5 a phase transition from tetragonal to a orthorhombic structure occurs, with a T_C of about 50K. At $y = 6.9$, the superconducting transition temperature increases to about 90K. As indicated in Fig.1 by the filled circle, the proposed low temperature deposition process (PE-MOCVD) is the first deposition process to form the orthorhombic superconducting phase in the as-deposited state. The filled circle in Fig.1 represents our present growth conditions. By further decreasing the deposition temperature, the in-situ formation of YBCO superconducting films with $y = 6.9$ will be possible and an in-situ, low temperature MOCVD growth process for $T_C \geq 90\text{K}$ HTSC thin films should result.

PE-MOCVD of YBCO using Nitrous Oxide

In PE-MOCVD, the presence of a plasma changes the chemistry of film formation from atom-atom to atom-ion or ion-ion, which is much more energetically favorable for compound formation. It has been shown that high quality films of a variety materials such as diamond and SiC can be deposited at significantly reduced temperatures using PE-MOCVD.^{8,9,10} The application of PE-MOCVD process to HTSC thin films should emerge as an exciting method to prepare oxide superconducting thin films with desired properties at much reduced deposition temperatures. $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ films prepared by PE-MOCVD at deposition temperatures as low as 580°C by and having $T_C = 82\text{K}$ and $J_C = 10^5\text{A/cm}^2$ at about 50K have recently been reported by Hitachi using oxygen as a reactant gas.¹¹ Nitrous oxide (N_2O) is known to be relatively inert to metalorganic precursors yet highly reactive when dissociated to atomic and ionic oxygen.^{12,13} Superconducting $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ films formed at 650°C by MOCVD using N_2O as reactant gas have been reported recently.¹⁴ Hence, by combining plasma activation and N_2O , we are seeking to develop a novel PE-MOCVD deposition technique for in-situ formation of superconducting high T_C oxide films at significantly reduced deposition temperatures. By employing higher microwave power levels (up to 500 W) and N_2O reactant gas, deposition temperatures as low as 400°C may be achieved. This technique will permit the deposition of high quality HTSC films on a variety of substrate materials such as Si and sapphire, which will have a significant impact on the early device applications of HTSC thin films.

Our preliminary work has demonstrated the feasibility of the proposed process. $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ superconducting films have been deposited, in-situ, at a substrate temperature of 570°C by PE-MOCVD using remote microwave (100W) plasma-activated nitrous oxide as a reactant gas. The use of a remote plasma avoids the direct, intense ion bombardment of the film surface. The deposition temperature was measured by a thermocouple in contact with the substrates.

PE-MOCVD System Development

A prototype EMCORE System 5000 MOCVD¹⁵ with a remote plasma coupling system was developed for the deposition of HTSC films. The system incorporated a resistance heated, high speed (0 - 2000 rpm) rotating-disk in a vertical, cylindrical cold wall growth chamber. The internal components of the reactor were chosen for their resistance to high temperature oxidation. The 5 inch diameter wafer carrier was configured to allow simultaneous growth on multiple substrates including (100) MgO, (1102) Sapphire, (100) SrTrO₃, YSZ, and Si wafers.

A N₂O plasma was generated by a 2.45 GHz microwave cavity mounted above the growth chamber with a special designed quartz injector tube which uniformly distributes the activated species. The cavity was powered by a modified microwave source with a variable power output of 10 - 100 Watts. Oxygen was uniformly introduced through the top of the chamber at 2 - 6 slm. The three precursors were transported by N₂ carrier gas, to individual dividing flow manifolds (injectors) mounted 120° apart. The separate injector arrangement for each source was chosen to minimize the possibility of gas phase reactions and to give additional degrees of freedom for optimizing compositional uniformity¹⁶. The vapor phase precursors were injected with a velocity of over 3 m/s. This high velocity significantly reduces the possibility of prereaction, resulting in a significant improvement in deposition efficiency.

Among the possible volatile organometallic precursors for high T_C MOCVD, metal β-diketonates are attractive since they are easily synthesized, purified, and handled in air. In order to form superconducting films in the as-deposited state, β-diketonate complexes Y(dpm)₃, Ba(dpm)₂, and Cu(dpm)₂ (dpm = dipivaloylmethanate), were used as yttrium, barium, and copper precursors, respectively. The bubblers for the copper and yttrium sources were specially designed to yield a constant mass transport rate since they are solid at these temperatures. Ba(dpm)₂ is the only known non-fluorocarbon-based β-diketonate complex which has significant volatility. However, Ba(dpm)₂ partially decomposes during the evaporation process, which causes its partial pressure to drop as a function of time at a constant source temperature. An apparatus for adding DPM ligand vapor to the source carrier gas was developed to stabilize the evaporation rate of [Ba(dpm)₂]₂, thereby ensuring that its vapor pressure remained constant.¹⁷ Also THF (tetrahydrofuran) was added to the Ba(dpm)₂ along with N₂ carrier gas to increase the volatility of Ba(dpm)₂. THF, which has a low boiling point and high volatility can attach to a conventional-diketone metal complex. All transport lines and valves were maintained at ≈10°C above the bubbler temperature to avoid decomposition or condensation of the precursors in the gas transport system.

Deposition was carried out at a system pressure of 10 - 76 Torr and substrate temperature of 550°C - 850°C with a rotation speed of 1100 rpm. After deposition, the films were slowly cooled to 100°C under one atmosphere of oxygen. Plasma power was 100W with 1.5 slm flow of N₂O gas. Film deposition rate was controlled at 0.5 - 1μm/hour and the films were usually 0.5 - 1μm thick.

YBa₂Cu₃O_{7-x} superconducting thin films with T_C above 90 K and J_C above 10⁴A/cm² were reproducibly deposited in-situ on YSZ substrate at 850°C in our MOCVD system. Fig. 2 is a variable temperature resistance measurement of an as-deposited film. It shows that this film has a metallic resistance behavior with extrapolation of the normal state resistance curve to zero resistance. This film has the onset of the superconducting transition at about 94K and attainment of zero resistance by 92K with a sharp transition width of 2K.

PE-MOCVD PROCESS

Carbon is a common impurity in films prepared by MOCVD processes, especially for films deposited at low temperatures. Fig. 3 is the Auger electron spectrum of the superconducting film formed at 610°C by PE-MOCVD with activated N₂O. With an instrumental sensitivity of 0.5 atomic percent, the barely detected carbon peak indicates that carbon content in the film is significantly less than one atomic percent. This result indicates great promise for this low temperature deposition technique. A smoothly dense film structure which is free of voids was obtained by the PE-MOCVD process, an important result for device technology. As shown in Fig. 4, the films show a sharp resistance transition, with a transition width of about 5K. However, the zero transition temperature of the initial films prepared by PE-MOCVD is 72K, which may be due to slight deviations in the film stoichiometry or to an oxygen deficiency in the film resulting from improper cooling.

Section 4.1 REFERENCES

1. S. Witanchchi, H.S. Kwok, X.W. Wang and D.T. Shaw Appl. Phys. Lett. 53, 234 (1988)
2. S. Prakash; D.M. Umarjee; H.J. Doerr.; C.V. Deshpadey and R.R. Bunshah Appl. Phys. Lett. 55, 31 (1989)
3. K. Mizuno, M. Miyauchi, K. Setsune and K. Wasa, Appl. Phys. Lett. 54, 383 (1989)
4. T. Aida, A. Tsukamoto, K. Imagawa, T. Fukazawa, S. Satito, K. Shindo, K. Takagi and K. Miyauch, Jpn. J. Appl. Phys 28, L635 (1989)
5. P. Zawadzki, G. Tompa, D. Noh, B. Gallois, C. Chern, and B. Kear, High Temperature Superconducting Technologies Symposium, Spring ECS Meeting, Los Angeles, May, 1989.
6. H. Yamane, H. Masumoto, T. Hirai, H. Iwasaki, K. Watanabe, N. Kobayashi and Y. Muto, Appl. Phys. Lett. 53, (1988) 1548; SUPERCONDUCTOR WEEK, 3, October 9, 1989.
7. R. H. Hammond and R. Bormann to be published in Appl. Phys. Lett.
8. M. Kamo, Y. Sato, S. Matsumoto, and N. Setaka, J. Cryst. Growth, 62, 642(1983).
9. A. Inspektor, U. Carmi, A. Raveh, Y. Weitzmann, N. Mayo, and R. Avni, Proc. of the Sixth European Conf. on CVD, edited by R. Porat (Iscar Ltd. Nahariya, Israel, 1987.
10. M. Shimizu, Y. Matsueda, T. Shiosaki and A.J. Kawabata, Crystal Growth 71, 209 (1985)
11. N. Sugii and K. Miyauchi, M7.172, MRS 1989 Fall Meeting Proceeding.
12. Handbook of Thin-Film Deposition Processes and Techniques, Noyes Publication (1988), Edited by K. Klaus K. Schuegraf.
13. X.D. Wu, A. Inam, M.S. Hegde, B. Wilkens, C.C. Chang, D.M. Hwang, L. Nazar, T. Venkatesan, S. Miura, S. Matsubara, Y. Miyasaka, and N. Shohata, Appl. Phys. Lett. 54, 754 (1989)
14. T. Tsuruoka, R. Kawasaki, and H. Abe, Jpn. J. Appl. Phys. 28, L607, 1989.
15. J. Zhao, D. Noh, C. Chern, Y.Q.Li, B. Gallois, P. Norris and B. Kear, submitted Appl. Phys. Lett.
16. G.S. Tompa, M.A. McKee, C. Beckham, P.A. Zadwadzki, J.M. Colabella, R.A. Stall, and P.E. Norris, J. Cryst. Growth 93 (1988) 220-227.
17. P.H. Dickinson, T. H. Geballe, A. Sanjurjo, D. Hildenbrand, G. Graig, M. Zisk, J. Collman, S.A. Banning, and R.E. Sievers, J. Appl. Phys, 66, 444, 1989.







